

**METALLACARBORANE-BASED PRECURSORS FOR
ELECTROACTIVE MATERIALS**

Final Report

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13. ABSTRACT (Maximum 200 words) This project was concerned with the design, preparation, and study of organometallic complexes containing transition metals, hydrocarbon rings, and boron-carbon (carborane) ligands, that can serve as precursors to new families of materials having useful electronic, magnetic, and/or optical properties. The work focused on three primary objectives: (1) design and synthesis of suitable metallacarborane building-block complexes; (2) development of methods for assembling large systems via linking, coupling, stacking, and fusion, and for chemically modifying the products; and (3) probing the electronic structures and properties of polymetallic species and developing correlations between properties and molecular structure. Efficient synthetic strategies were developed for preparing a variety of stacked and/or linked multilayers and multidecker complexes, and for modifying these via introduction of functional groups at specified locations. In addition, the electronic and magnetic properties of a number of selected species were investigated in detail, with particular interest on electron-delocalization and communication between metal centers.				
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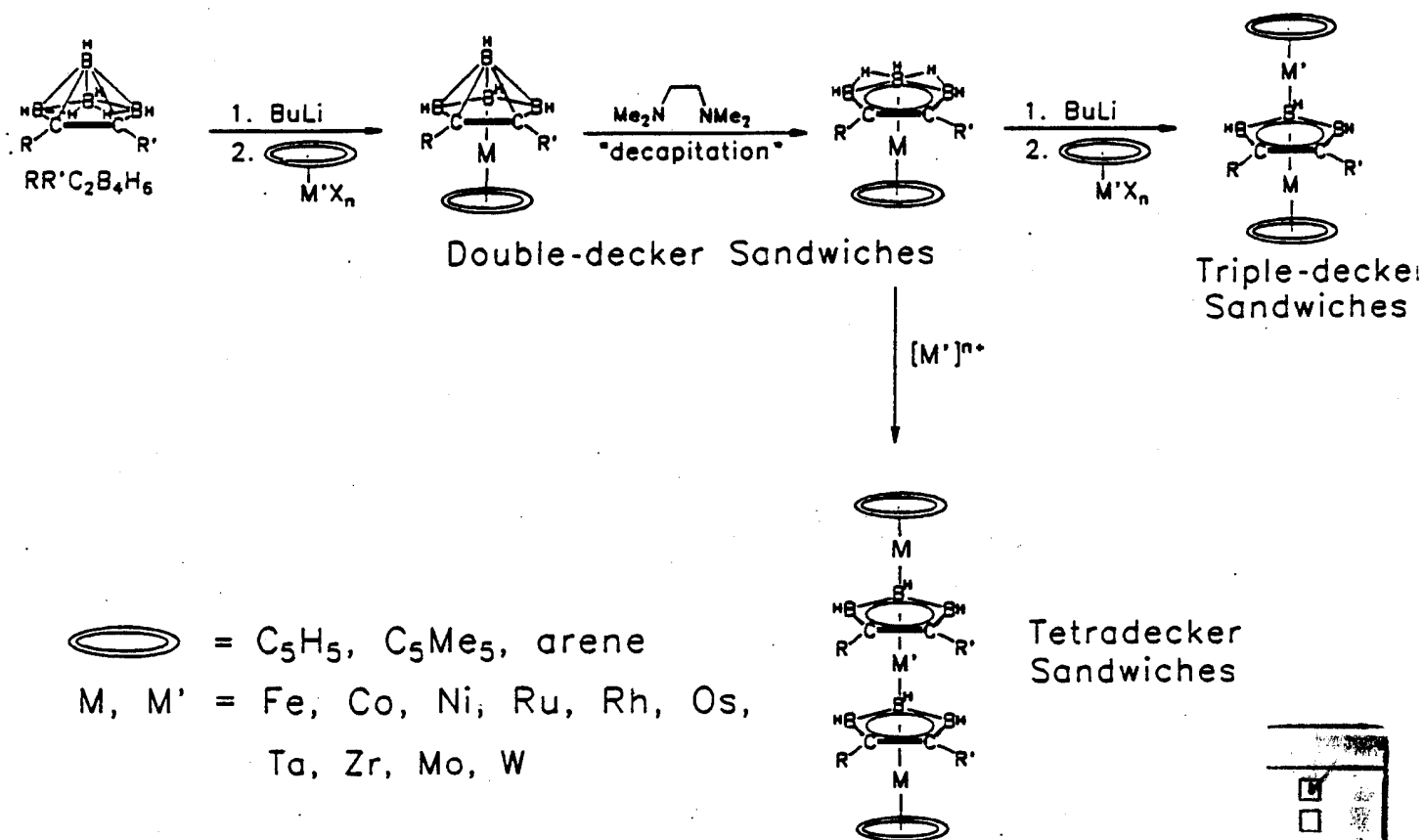
I. Statement of Problem

This project centered on the design, preparation, and study of organometallic complexes containing transition metals, hydrocarbon rings, and boron-carbon (carborane) ligands, that can serve as precursors to new families of materials having useful electronic, magnetic, and/or optical properties.

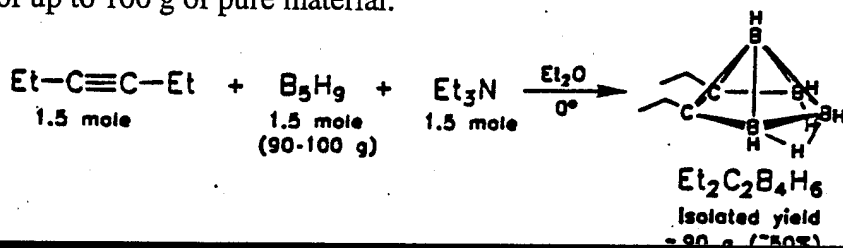
II. Summary of Important Results

1. Multigram-Scale Synthesis of Nido-Metallacarborane Synthons

The starting point for much of this chemistry is the preparation of double-decker metallacarborane complexes of types $LM(RR'C_2B_4H_6)$ and nido- $LM(RR'C_2B_3H_5)$ from $RR'C_2B_4H_6$ nido-carboranes, which in turn are used to build higher multidecker stacks as shown.



Our new multigram-scale procedure for preparing the $Et_2C_2B_4H_6$ carborane starting material from B_5H_9 and alkynes under safe conditions, has been further improved to allow the synthesis of up to 100 g of pure material.

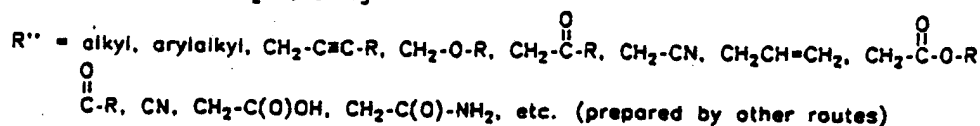
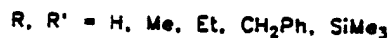
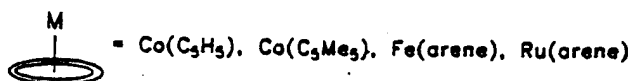
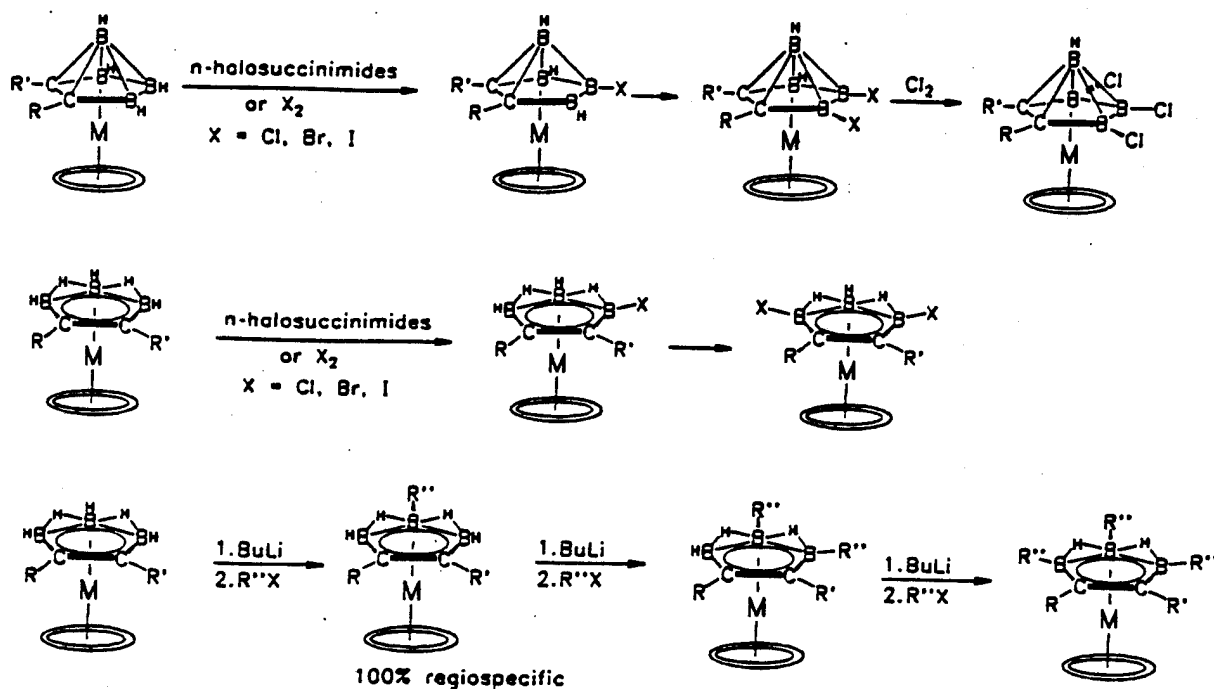


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Other carborane derivatives can be similarly obtained using commercially available or readily prepared alkynes. The accessibility of these carboranes in large quantity in turn allows us to make the double-decker sandwich building-block complexes on a multigram scale, as needed.

2. Derivatization of Small Metallocarborane Synthons

Systematic procedures were developed for introducing a wide variety of organic and inorganic substituents at designated boron and carbon locations on the carborane ligands and on the metal centers, thereby allowing tailoring of the reactivity of these complexes via electronic and/or steric effects.

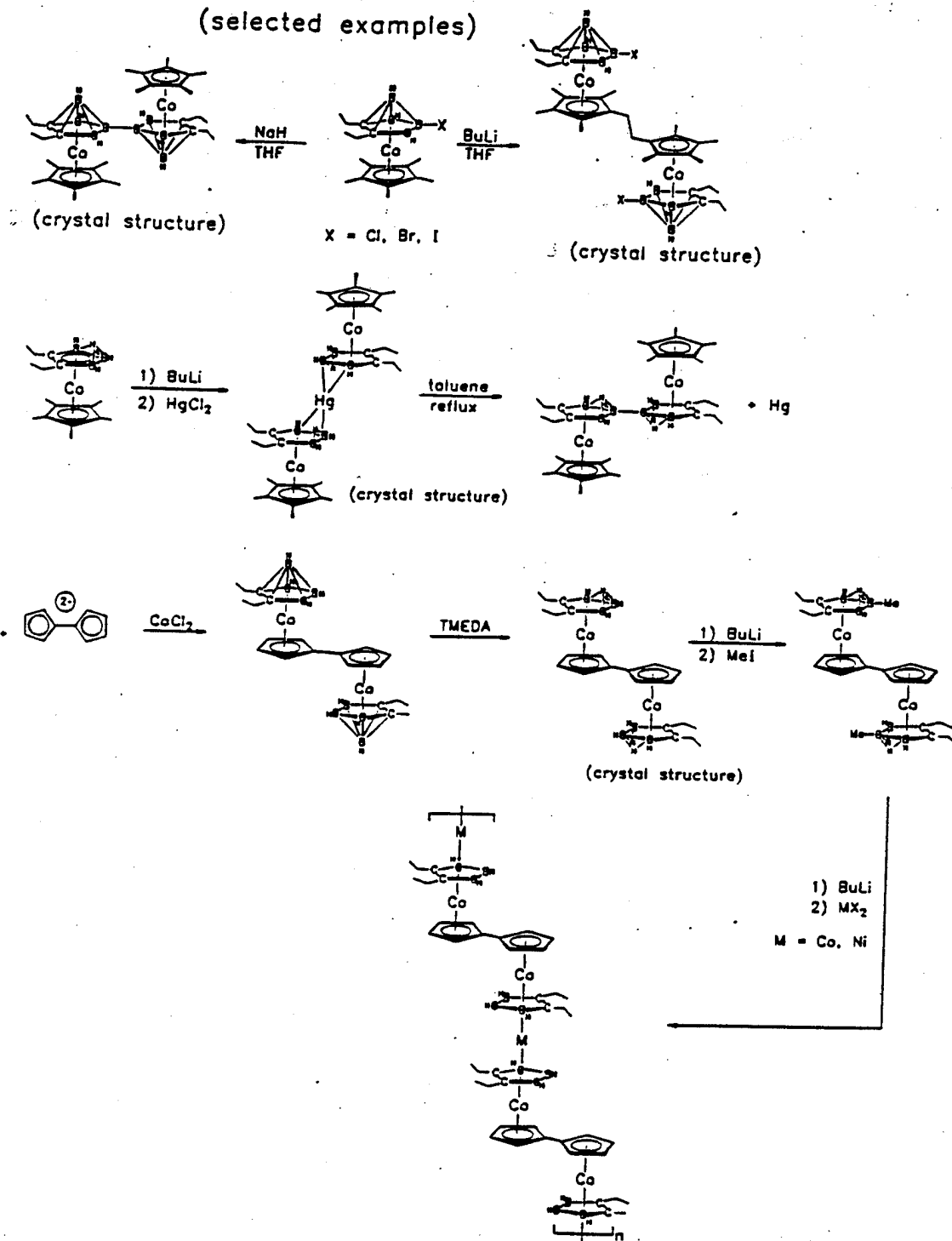


3. Assembly of Multimetallic Systems

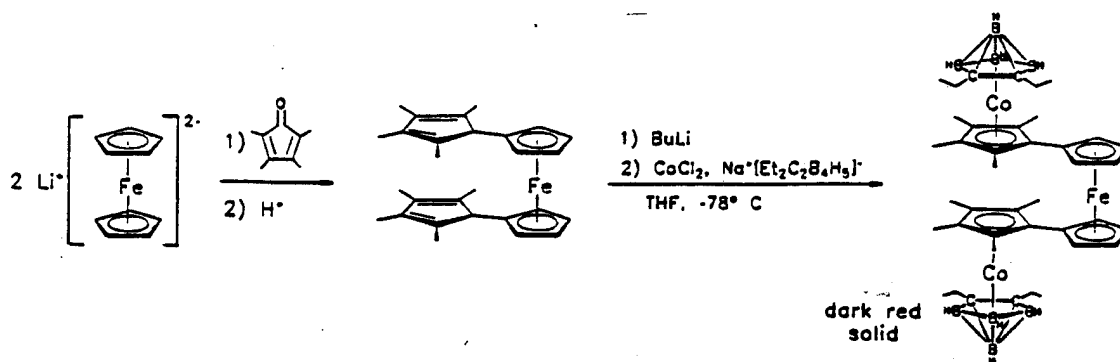
Two parallel strategies have been followed for assembling macromolecules from small metallocarborane synthons.

Linkage of sandwich or cluster units via carborane-carborane, hydrocarbon-hydrocarbon, or metal-metal coupling. The methods shown have been employed to achieve direct B-B intercage bonding as well as Cp-Cp, Cp*-Cp*, or metal-metal linkage, generating dimers or oligomers that are useful synthons for building large systems.

(selected examples)

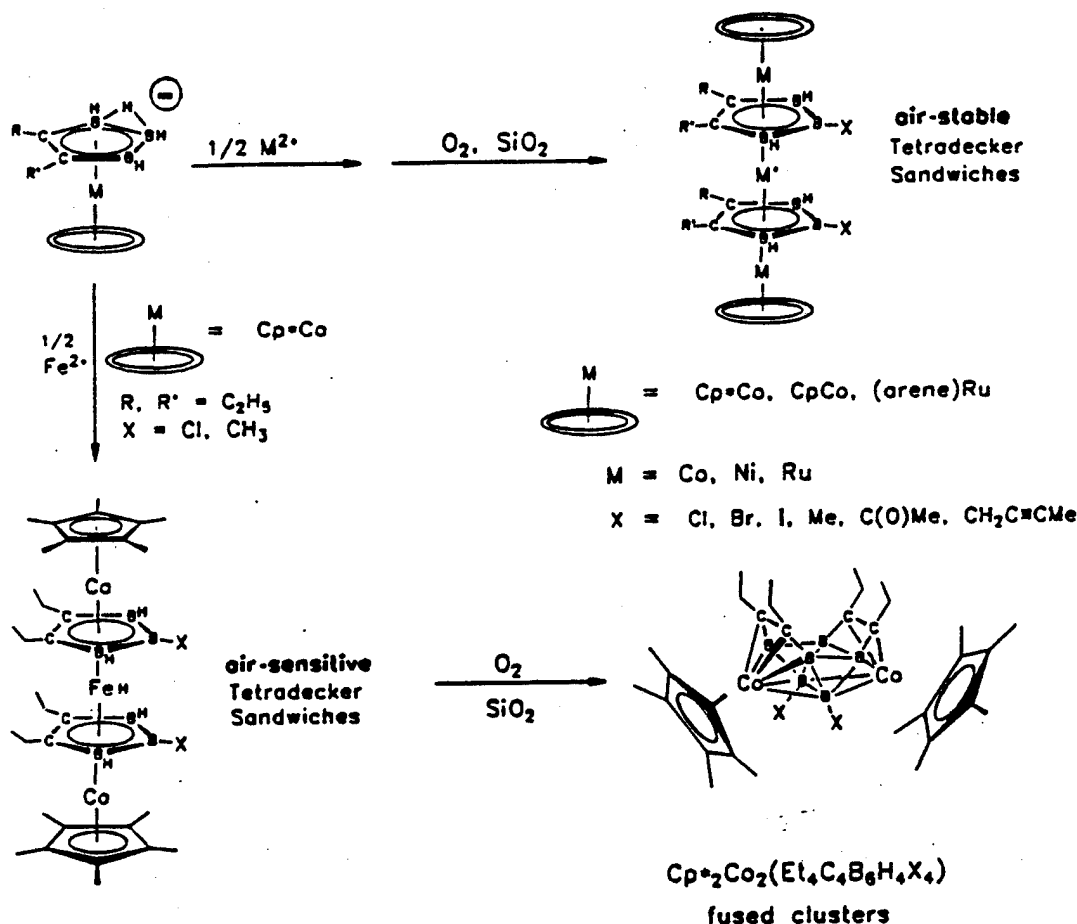


Ferrocene-cobaltacarborane "hybrid" and metal-metal bonded complexes represent another type of linked system that has been investigated:

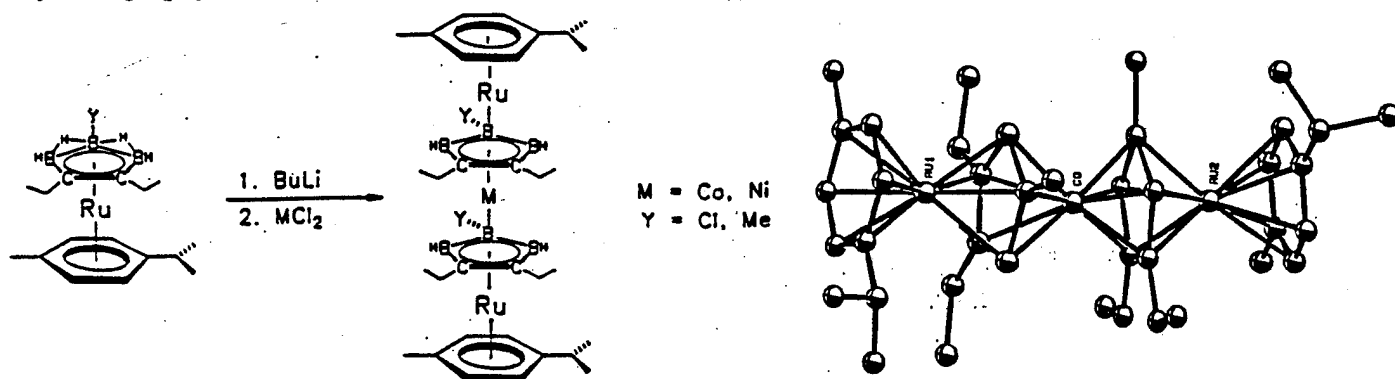


Multidecker stacking. Significant advances during this Contract period, extending our two decades of pioneering in this area, include (1) elucidation of the influence of substituents and workup conditions on the stacking mechanism vs. competitive processes such as cage fusion; (2) the isolation of Fe-centered tetradeckers, elusive species that generate fused clusters under normal workup conditions; (3) the synthesis of [(arene)Ru(RR'C₂B₃H₃)]₂M sandwiches (the first carborane tetradeckers featuring end units other than Cp*Co); (4) the preparation of penta- and hexadecker sandwich complexes and the first structurally characterized examples of the latter; and (5) synthesis of C₂B₃-endcapped tetradeckers for use in our current attempts to construct octadecker complexes.

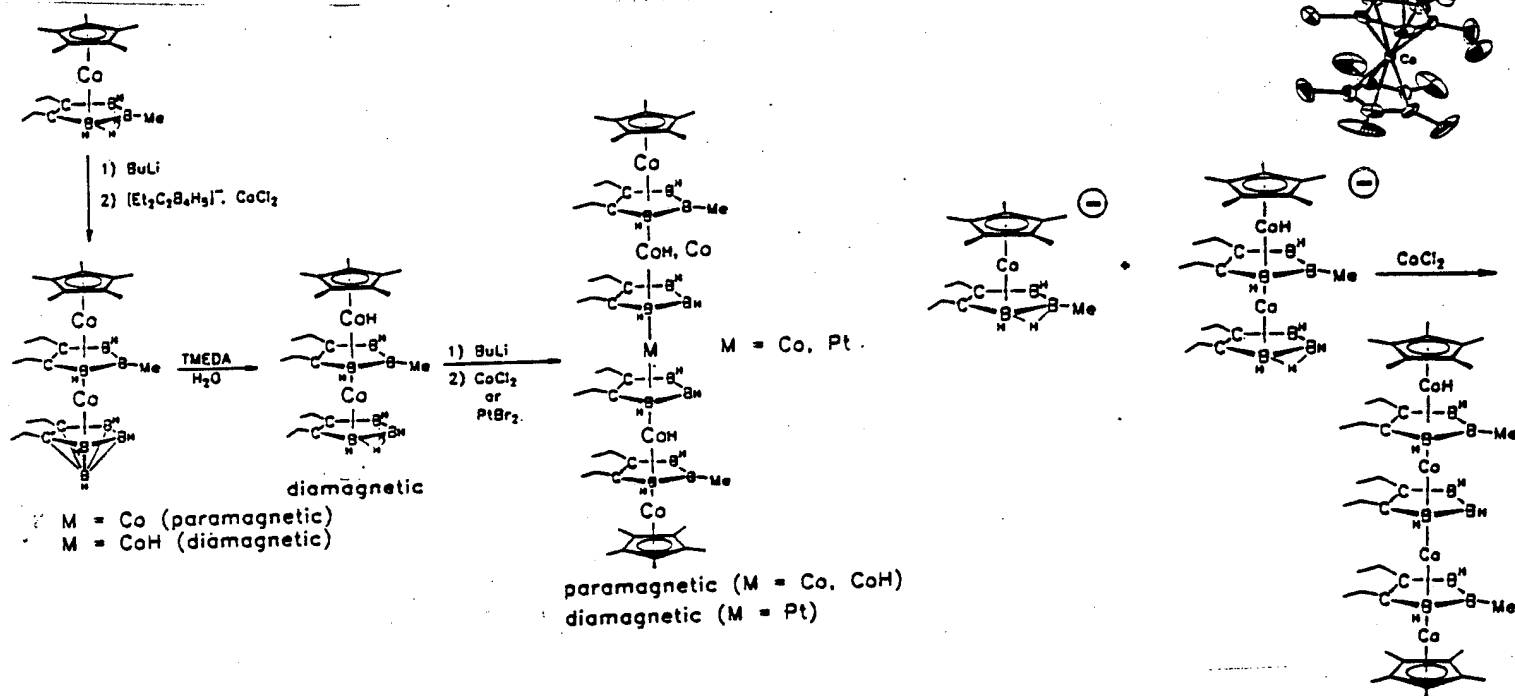
As shown, air-sensitive iron tetradeckers were isolated by avoiding contact with silica in air. Chromatography on silica afforded instead fused clusters via oxidative fusion.



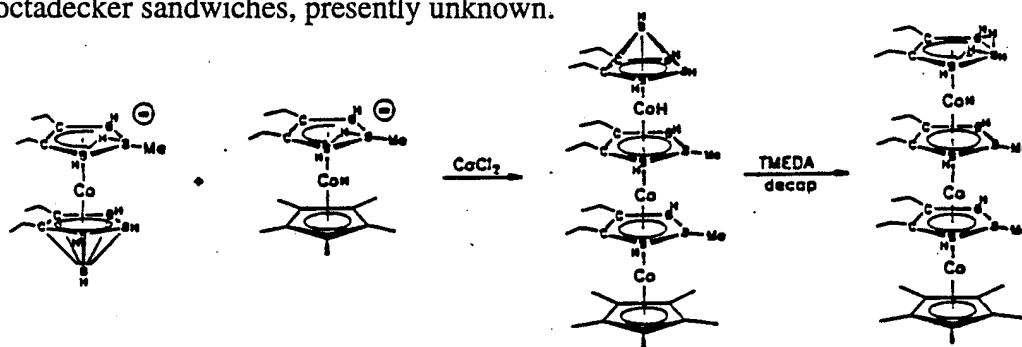
The preparation of Ru-Co-Ru and Ru-Ni-Ru tetradecker sandwiches depicted below represents the first use of a synthon other than (C₅R₅)Co(RR'C₂B₃H₃) in the preparation of carborane tetradeckers, and hence extends our stable of available building-block reagents for multidecker synthesis. Three of these species were structurally characterized via X-ray crystallography, and the structure of [(MeC₆H₄iPr)Ru(Et₂C₂B₃H₂Me)]₂Co is illustrated.



Extension of the metal-stacking reaction to larger sandwiches required triple-decker synthons featuring open C_2B_3 end rings which were prepared and subsequently employed to make pentadecker and hexadecker complexes. This strategy required the attachment of a halogen or alkyl group on the C_2B_3 ring in the $Cp^*Co(Et_2C_2B_3H_4X)$ starting complex in order to inhibit fusion, and promote formation of the target sandwiches, as shown. In addition to the pentacobalt paramagnetic species, which have respectively one and two unpaired electrons as shown by ESR measurements, a diamagnetic Pt-centered hexadecker has also been prepared. The Co_5 hexadecker complex illustrated at right is the largest known crystallographically established multidecker sandwich.



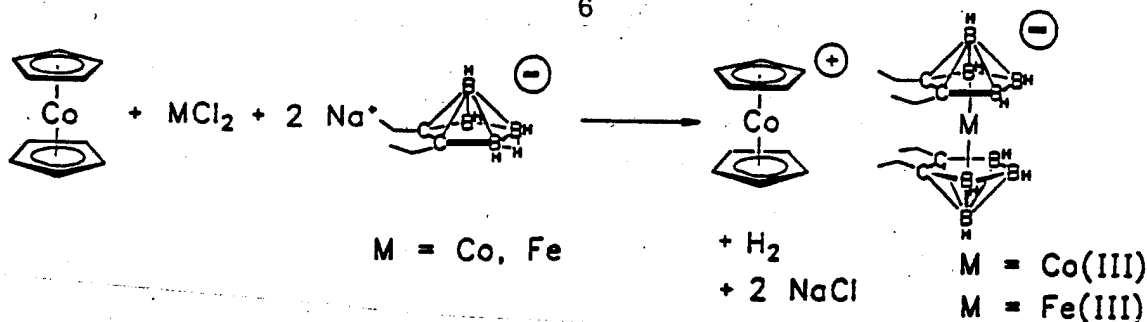
The route shown below was developed to generate tetradecker species having open carborane end rings. Such complexes are expected to undergo metal stacking reactions to form hepta- and octadecker sandwiches, presently unknown.



4. Synthesis of Solid-State Compounds and Molecular Precursors

Complementary to the molecule-based chemistry just described, a parallel effort has been directed at incorporating metallacarborane or related metal-boron clusters in solid state materials.

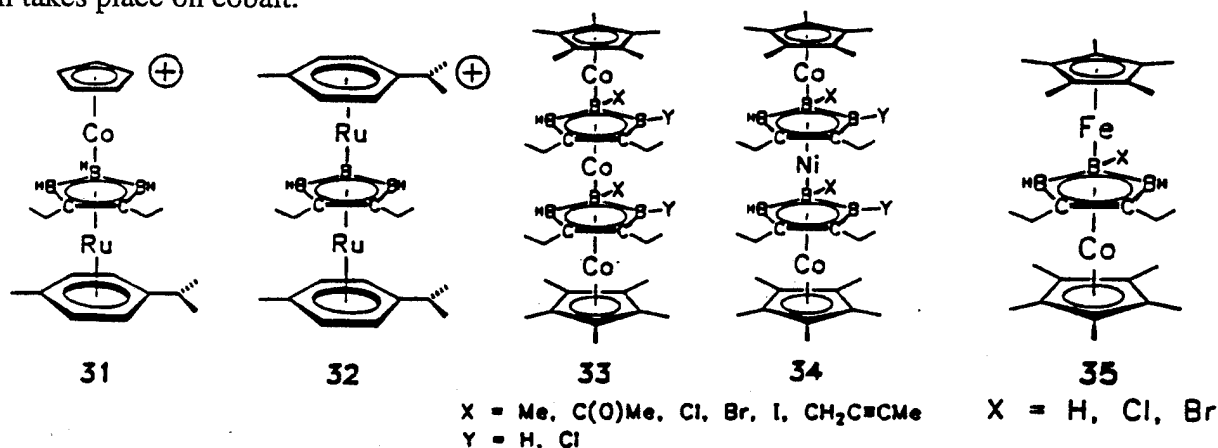
Metallocenium metallacarboranide salts. The isoelectronic/isosteric analogy between carborane anions and $C_5R_5^-$ ions has been exploited by the preparation and structural characterization of the first cobaltocenium-metallacarboranide salts. Such materials may ultimately be tailored to create tailored to create stacked arrays that allow low-dimensional electron delocalization.



The thermolysis of selected metallacarborane monomers has also been explored as a route to solid state materials, using relatively low temperatures (ca. 400-800 °C) in an attempt to remove exopolyhedral ligands while *retaining the cluster framework*, thereby inducing condensation to form three-dimensional solid networks.

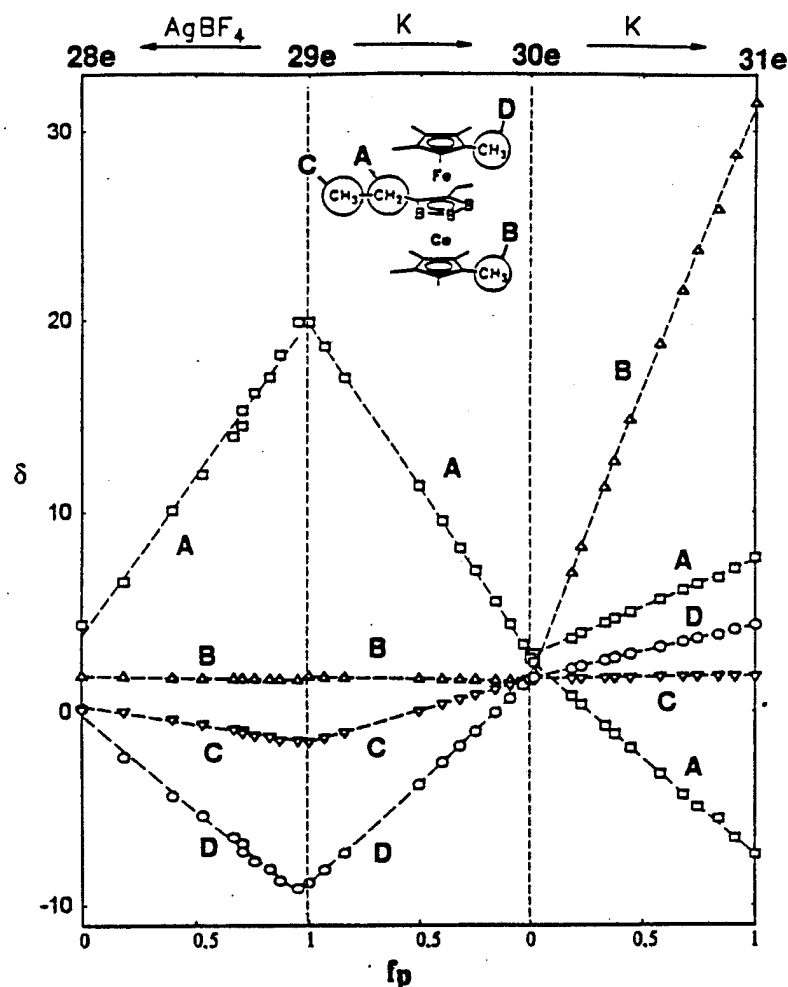
5. Studies of Electronic Structure and Properties

In order to explore the question of electron-delocalization between metal centers in polymetallic species, spectroelectrochemical investigations in collaboration with W. E. Geiger and coworkers have been conducted on the paramagnetic triple-decker sandwich cations typified by those shown below. $\text{Cp}^*\text{Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Ru}(\text{MeC}_6\text{H}_4\text{iPr})^+$ and $(\text{MeC}_6\text{H}_4\text{iPr})\text{Ru}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Ru}(\text{MeC}_6\text{H}_4\text{iPr})^+$ were demonstrated to be Class III (fully delocalized) mixed-valence species; similarly, cyclic voltammetry and controlled potential electrolysis on a series of Co-Co-Co and Co-Ni-Co tetradeccker complexes gave strong indication of extensive delocalization in these systems. In contrast, ESR and paramagnetic correlated NMR studies on the iron-cobalt triple-decker complex shown are consistent with highly *localized* electronic states; oxidation and reduction of the paramagnetic 29-electron neutral species occur exclusively at the iron center, while reduction of the diamagnetic 30-electron monoanion takes place on cobalt.



Electron delocalization in linked-sandwich multimetallic complexes has also been examined, revealing that phenylene-connected complexes show little or no electronic communication *between* the sandwich units, almost certainly because of the tilt (ca. 40°) between the phenylene ring and the adjacent cyclopentadienyl rings which prevents π -conjugation. However, fulvalene-based oligomers exhibit preliminary evidence of inter-sandwich electron delocalization. In very recent work on these complexes, a new technique, spectroelectrochemical infrared spectroscopy, has been added to the arsenal. Collaborative work with Geiger's laboratory on dicobalt fulvalene complexes has demonstrated that successive one-electron reductions of the neutral species to the dianion produce a very large (80 cm^{-1}) total shift in the B-H stretching frequency, equally partitioned between the two steps and thus establishing a delocalized electronic structure. More generally, we have demonstrated that the effect is a sensitive diagnostic tool for probing delocalization.

In addition to cyclic voltammetry, ESR, and UV-visible spectroscopy, another technique we have used to probe electronic structure is that of correlated NMR spectroscopy. In this method, which our laboratory has pioneered in cooperation with the Heidelberg group, ^1H or ^{13}C NMR spectra of paramagnetic species are completely assigned via stepwise reduction or oxidation of the initial species, with the spectrum recorded at each stage. This produces a linear plot for each signal as a function of f_p , the fraction of paramagnetic species in solution, and hence allows correlation with the diamagnetic spectrum (in which the assignment of resonances is usually straightforward). The diagram below depicts changes in the proton chemical shifts (δ) for the Fe-Co triple-decker complex illustrated, a 29-electron paramagnetic neutral system, as it undergoes oxidation to the diamagnetic cation and reduction to a diamagnetic monoanion and a paramagnetic dianion. Consistent with electrochemical findings, these data establish that this system has a localized structure (no metal-metal communication), in sharp contrast to the fully delocalized Co-Ru and Ru-Ru triple-deckers.



III. Publications produced under this Contract

173. M. A. Benvenuto and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 28. Controlled Substitution at Cage Carbon Atoms in CoC_2B_4 Clusters. Linkage of Bis(cobaltacarborane) Sandwich Complexes via Carbon-Bound Bridging Groups", *Inorg. Chem.* **1992**, *31*, 3897.

174. M. A. Benvenuto, M. Sabat, and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 29. Synthesis of Selectively C- and B-Substituted Double- and Triple-Decker Sandwiches. $(\eta^5\text{-C}_5\text{Me}_5)\text{Co}^{\text{III}}(\eta^5\text{-R}_2\text{C}_2\text{B}_3\text{R}'_3\text{H}_2)$ Cobaltocenium Analogues", Inorg. Chem. 1992, 31, 3904.
175. K. W. Piepgrass, Xiangsheng Meng, M. Hölscher, M. Sabat, and R. N. Grimes, "Tetradeccker Metallacarborane Sandwiches: Synthesis via Double-Decker Stacking and Structural Characterization of Co-Co-Co, Co-Ni-Co, and Co-Ru-Co Complexes", Inorg. Chem. 1992, 31, 5202.
176. J. W. Merkert, J. H. Davis, Jr., W. E. Geiger, and R. N. Grimes, "Delocalization in Bimetallic Triple-Decker Complexes: Electrochemistry, ESR Spectroscopy, and Spectroelectrochemistry of $(\text{p-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_2(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)$ and $\text{CpCo}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Ru}(\text{p-MeC}_6\text{H}_4\text{CHMe}_2)$ and Derived Ions", J. Am. Chem. Soc. 1992, 114, 9846.
177. K. W. Piepgrass, M. Curtis, X. Wang, X. Meng, M. Sabat, and R. N. Grimes, "Carbon-Rich Metallacarboranes. 15. Novel Metal-Promoted Cluster Fusion Reactions", Inorg. Chem. 1993, 32, 2156.
178. X. Meng, S. Waterworth, M. Sabat, and R. N. Grimes, "Cobaltocenium Metallacarboranide Mixed-Sandwich Salts, $\text{Cp}_2\text{M}^+(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)_2\text{MH}_n^-$ ", Inorg. Chem., 1993, 32, 3188.
179. X. Meng, M. Sabat, and R. N. Grimes, "Metallacarborane Staircase Oligomers. Stepwise Assembly via Tetradeccker Stacking Reactions", J. Am. Chem. Soc., 1993, 115, 6143.
180. J. R. Pipal and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 32. Electrochemical and Electron Spin Resonance Studies of Tetradeccker Sandwich Complexes", Organometallics, 1993, 12, 4452.
181. J. R. Pipal and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 33. Electrochemistry of Polymetallacarborane Staircase Oligomers", Organometallics, 1993, 12, 4459.
184. M. Stephan, P. Müller, U. Zenneck, R. N. Grimes, and W. Siebert, "Paramagnetic Metallacarborane Complexes. Synthesis, Electrochemistry, ESR, and P-NMR Studies", *Current Topics in the Chemistry of Boron*, Kabalka, G. W., Ed., Royal Society of Chemistry, Cambridge, 1994, 326.
185. J. R. Pipal and R. N. Grimes, "Electrochemistry of Tetradeccker Metallacarboranes", *Current Topics in the Chemistry of Boron*, Kabalka, G. W., Ed., Royal Society of Chemistry, Cambridge, 1994, 318.
186. X. Wang, M. Sabat, and R. N. Grimes, "Synthesis and Structure of a Hexadecker Sandwich", J. Am. Chem. Soc. 1994, 116, 2687.
188. M. Stephan, J. Hauss, U. Zenneck, W. Siebert, and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 35. Electrochemistry, ESR, and Correlated NMR Spectroscopy of Paramagnetic Mono- and Dinuclear $\text{Cp}^*\text{CoC}_2\text{B}_4$ Clusters", Inorg. Chem. 1994, 33, 4211.

189. R. N. Grimes, "Cluster Forming and Cage Fusion in Metallacarborane Chemistry", *Coord. Chem. Rev.* 1995, 131, 0000.
190. T. T. Chin, S. R. Lovelace, W. E. Geiger, C. M. Davis, and R. N. Grimes, "Infrared Spectroelectrochemistry of Boron-Hydrogen Stretches: A New Tool for Diagnosis of Delocalization in Mixed-Valent Metallacarborane Complexes", *J. Am. Chem. Soc.* 1994, 116, 9359.
191. M. Stephan, P. Müller, U. Zenneck, W. Pritzkow, W. Siebert, and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 37. Studies of Paramagnetic Iron-Cobalt and Dicobalt Triple-Decker Sandwich Complexes", *Inorg. Chem.* 1995, 34, 2058.
194. P. Greiwe, M. Sabat, and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 39. Arene-Capped Ruthenium-Carborane Tetradecker Sandwich Complexes", *Organometallics* 1995, 14, in press.
195. R. N. Grimes, "Metal-Carborane Multidecker Sandwich Complexes as Building-Blocks for New Materials", *Appl. Organometallic Chem.*, in press.
196. K. E. Stockman, D. L. Garrett, and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 40. Regiospecific Halogenation of Transition Metal Small Carborane Complexes", in press.
197. X. Wang, M. Sabat, and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 41. Synthesis and Structure of B-B and Cp*-Cp* Linked Cobaltacarborane Clusters", in press.
198. X. Wang, M. Sabat, and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 42. Synthesis and Cluster Fusion of Iron-Centered Tetradecker Sandwiches", submitted for publication.

IV. Participating Scientific Personnel

Principal Investigator: Russell N. Grimes, Professor of Chemistry

Postdoctoral Associates:

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Craig Davis

Graduate Students (degrees earned):

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Xiaotai Wang (Ph. D. May 1995)
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